Effect of Electrolytes on the Distribution of Trichloroacetic Acid between Butanol and Water

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(Received 25th April, 1991, revised 17th October, 1991)

Summary: The distribution of trichloroacetic acid between the aqueous and organic phase containing varying amounts of electrolytes was studied at room temeprature 25°C ± 1. A correlation was derived between the distribution of acid and ionic strength of the partitioning medium. It was found that in the presence of anions I^-, Cl^-, Br^-, SO_4^-, and cations Na^+, K^+, Ba^{++}, the distribution coefficient of acid increased gradually with increase in the concentration of both groups of ions. However in the presence of F^- and Al^{+3} a reverse effect on the distribution of acid was observed.

Introduction

Determining with convenience the partition coefficient or distribution character of chemical and biochemical substances is becoming increasingly important in separation science extraction procedures and isolation purification disciplines [1,2]. Extraction of organic and inorganic substances from crude materials can be easily achieved by shaking their solutions with an immiscible solvent. The distribution law [3] requires that at equilibrium, the ratio of concentrations in two layers at constant temperature should be constant provided the solute does not approach or exceed its solubility. A literature search [4,5,6] of the distribution of trichloroacetic acid (TCA) has revealed that no significant work has been reported on the distribution TCA in the presence of electrolytes. Therefore these investigations were undertaken for a better understanding of the effect of electrolytes on the distribution of TCA between immiscible solvents and with a view to study the characteristics of butanol which are being used increasingly in extractive metallurgy and also for extraction of phosphoric acid in the presence of calcium chloride, hydrochloric acid and chlorides of iron, aluminium and magnesium.

Results and Discussion

The results of our investigations on the distribution of TCA in the presence of cationic and anionic electrolytes are presented in Table 1 and 2. Before discussing these results it is pertinent to consider the existing hypothesis regarding the distribution of TCA between immiscible liquids. It has been reported by Findlay [4] *et al.* (1981) that the distribution behaviour of TCA is very erratic and does not follow a regular pattern. Similar findings have been also reported by Zaheer-ud-Din [7] and Lodhi (1985). According to Bonner [5] *et al.* (1972) TCA forms an ion pair in the aqueous phase and association to form dimers may occur in the other phase.

Table 1: Effect of electrolyte concentration on the distribution, coefficient of TCA

Conc. of Salt (m)	Distribution coefficient of TCA in the presence of			
	NaCl	NaBr	KI	Na_2SO_4
0.1	5.22	5.05	5.43	1.52
0.5	5.23	6.04	5.60	1.74
1.0	5.76	6.59	5.64	1.83
1.5	5.91	6.88	5.89	1.93
2.0	6.33	6.88	5.98	-
2.5	6.75	6.91	6.02	-

Table 2: Effect of electrolyte concentration on the distribution coefficient of TCA

Conc. of NaF (M)	K	Conc. of $BaCl_2$ (M)	K	Conc. of $AlCl_3$(M)	K^a
0.1	5.82	0.2	4.11	0.1	4.39
0.02	5.72	0.4	4.31	0.3	4.35
0.03	5.54	0.6	4.83	0.5	4.33
0.04	5.38	0.8	4.85	1.0	4.32
0.5	5.37	1.0	4.87	1.5	4.30
0.06	5.37				

The observed distribution coefficients of TCA between butanol and water listed in Table 1 and 2 suggests that with the exception of sodium halides, other halides have increased the distribution of the TCA and followed a regular pattern. In the presence of sodium fluoride, it appears that the salt solutions are somewhat dilute and that salting in effect may be taking place. As a consequence more acid will be retaining in the aqueous layer as compared to organic layer. Furthermore the high solubility of TCA in the aqueous phase may also be due to high electronegativity of fluoride. Therefore causing a decrease in the solubility of acid in the organic phase.

With other sodium halides, the distribution coefficient of TCA increased regularly with the increase in electrolyte concentrations. These findings suggest that the addition of electrolytes to the partitioning medium has caused a decrease in the solvation of TCA in the aqueous layer, probably due to salting out effect. The observed distribution coefficients of TCA in the presence of sodium chloride, sodium bromide and sodium iodide are consistant with the earlier findings [8,9] undertaken in a different system. These investigators have studied the effect of electrolytes on the distribution of malonic acid between 1- pentanol and water, and rationalised the effect of sodium halides to their ionic radii. According by the increasing order of effectiveness of sodium halides on distribution was found to be $I^- > Br^- > Cl^-$.

The present investigations on the distribution of TCA between butanol and water in the presence of sodium halides not only confirm the earlier findings [8,9] but also provide additional evidence on the effectiveness of sodium halides during the partitioning of exogenous chemicals between immiscible liquids. Apart from studying the effect of sodium halides on the distribution character of TCA, the effects of sodium sulphate and barium chlorides were also investigated. As evident from the results Table 2 both chemicals have influenced the distribution of TCA because of the salting out effect which was more prominent in case of barium chloride than sodium sulphate.

In the presence of aluminium chloride, as clear from the result Table 2, a salting in phenomenon, similar to that occured. With sodium fluoride, the distribution of the acid decreased gradually with increasing concentration of aluminium chloride. The result suggests that the unique behaviour of aluminium chloride on the distribution of TCA can be due to either high negative charge on the chloride ion or high positive charge on the aluminium ion. Further studies can be undertaken to quantify the effect of aluminium chloride on the distribution of TCA between the aqueous and organic phase.

Experimental

Chemicals

Trichloroacetic acid and butanol were obtained from E. Merck, sodium chloride, sodium bromide, sodium sulphate, barium chloride, aluminium chloride, potassium iodide, potassium acid phthalate were Analar grade, obtained from DDH Ltd., Poole U.K. All other chemicals and reagents were of highest purity. Solvents were of standard laboratory grade redistilled before use.

Method

The following standard solutions of electrolytes were prepared in distilled water.

1. 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 M solutions of sodium fluroide.
2. 0.1, 0.5, 1.00, 1.5, 2.0, 2.5 M solutions of sodium chloride.
3. 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 M solutions of sodium bromide.
4. 0.1, 0.5, 1.0, 1.5 M solutions of aluminium chloride.
5. 0.2, 0.4, 0.6, 0.8, 0.1M solution of barium chloride.
6. 0.1, 0.3, 0.5, 1.0, 1.5 M solution of aluminium chloride.
7. 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 M solutions of potassium iodide.
8. 0.4, 0.6, 1.0 M solutions of trichloroacetic acid were prepared using the above electrolyte solutions as solvent.

The partitioning system comprised butanol and 0.4, 0.6, 1.0 M solutions TCA (25 = 25 ml). Before partitioning, each phase was saturated with the other. Distribution coefficients of trichloroacetic acid solutions were determined by the shake flask method (Zaheer-ud-Din and Lodhi, 1985 [7]. The two phaše were transferred to a separating funnel and vigorously shaken for 2 hours at room temperature 25°C ± 1. Later both phases were allowed to stand and then carefully separated. 5 ml aliquots from each layer were withdrawn and titrated in duplicate against standard sodium hydroxide solution using phenolphthalein as an indicator.

The concentrations of trichloroacetic acid in the aqueous and organic layers were determined and the distribution coefficient were determined using the formula $Co/CW = K$ where Co and CW were the concentrations of the acid in the butanol and water layers respectively and K the distribution coefficient.

Conclusion

We believe that the results presented, clearly demonstrate the effectiveness of electrolytes on the distribution and extraction of exogenous chemicals between immiscible liquids. Optimum conditions for selective extracting and purifying desired chemical from crude mixtures can be chosen, therefore the implication of these results need to be borne in mind while devising distribution coefficient experiments of exogenous chemicals in the presence of endogenous electrolytes.

References

1. F. Daniels, J.W. Williams, P. Bander, R.A. Alberty, 1962. Exp. Physical Chemistry, 6th ed., Mc Graw-Hill, New York.
2. J. Talgyessy, T. Braum, T. Kyrs. 1972. Isotope Dilution Analysis, Pergamon Press Oxford.
3. D.R. Reese, G.M. IrNin, L.W. Dittert. C.W. Chong, J.V. Swintosky, *J.Pharm.Sci.,* **53**, 591 (1964).
4. T.J.V. Findlay, P.D. Lark, R. Nobes, R.G. Peterson, N. Ramos, *Proc. Sec. Australian Thermodyn Conf. Melbourne* (1981).
5. O.D. Bonner, H.B. Flora, M.W. Aitken, *J.Phy.Chem.,* **75** 2492 (1972).
6. N.S. Zaugg, A.J. Kellay, E.M. Wolley, *J.Chem.Engg.Data* **24**, 218 (1979).
7. M. Zaheeruddin, and Z.M. Lodhi, *Phy.Chem.,* **4**, 53 (1985).
8. M. Zaheeruddin, F. Rahim, M.Sc. Thesis University of Peshawar (1980).
9. G. Nawab, M. Sc. Thesis, University of Peshawar (1978).